LALP-08-048
Summer 2008

MATERIALS RESEARCH HIGHLIGHT

Metallic nanolayered composites exhibit ultra-high strength and ductility

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Recently, the high strength of nanomaterials has gathered much interest in the materials community. Polycrystalline and composites nanomaterials are used, largely by the semiconductor community, where critical length scales for chip design have decreased to tens of nanometers. To ensure reliability of nanomaterials in other applications, however, the mechanisms underlying their structural integrity must be well understood; not only should strength be considered, but also ductility, toughness, formability, and fatigue resistance. While some progress has been made into constructing models for such deformation mechanisms, little experimental research exists, especially when length scales drop below 10 nanometers (nm). This work forges new inroads into some of these areas by producing stress-strain curves for nanolaminate composites with individual layer thickness of 40 and 5 nm. Nanolaminate composites fabricated via magnetron sputtering, comprised of alternating 5 nm thick Cu and Nb multilayers (two relatively soft metals), exhibit strengths on par with tool steel and deformability in compression in excess of 25%[1].

Some of the challenges in evaluating the stress-strain response of nanomaterials involve the fabrication of flaw-free samples that will reliably give mechanical test data reflecting the bulk material properties independent of geometric effects of sample size or embedded flaws. Magnetron sputtering at the Center for Integrated Nanotechnologies provides for fabrication of metallic multilayers such that (i) the growth-induced residual stresses and flaws/porosity are minimized, (ii) the individual layer thicknesses are well-controlled in the nanometer range, and (iii) the overall sample thickness is sufficient to make self-supported foils. This precise control over length scales allows for systematic investigation of the effects of increasing the amount of interfacial content on material behavior. Figure 1 is a cross-sectional transmission electron micrograph (TEM) of a sample with 5-nm layer thickness, although layers of alternating Cu and Nb can be easily varied in thickness to investigate length scales (and accompanying deformation mechanisms) from hundreds of nanometers to ~1 nm in samples with identical chemical composition. The laminar nature of the composites is evident from the micrograph, with the (111) planes of fcc-Cu and (110) planes of bcc-Nb forming the interface between the two phases, as shown in the diffraction pattern embedded selected area.

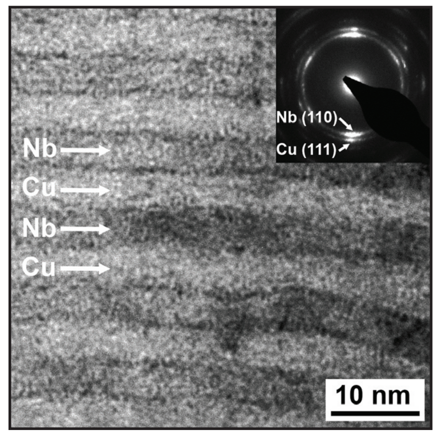

Figure 1: TEM bright-field (defocused to emphasize Z-contrast) micrograph of as-deposited 5 nm Cu/5 nm Nb. Note selected area diffraction pattern showing {111} Cu||{110} Nb fiber texture.

Once deposited, nanolayered composites can be deformed utilizing a variety of methods, including rolling[2], tension[3], indentation[4], or as in this case, micropillar compression. Focused ion beam (FIB) machining has opened opportunities for fabrication of micropillar samples, where a Ga^+ ion beam is used to remove material to shape a sample to high precision.[5,6] The inset scanning electron microscopy (SEM) micrograph in Figure 2 shows such a pillar with nominal dimensions of a diameter of 4μm and a height of 8μm. The layer direction is perpendicular to the cylinder axis,

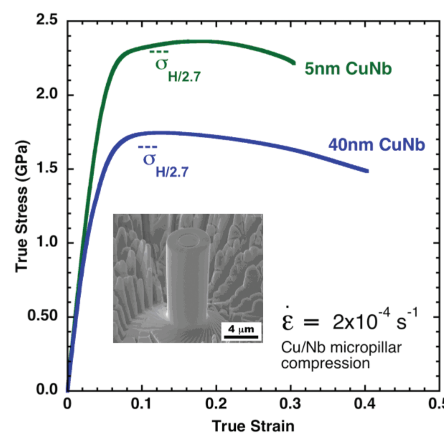

Figure 2. Compression curves for 40-nm and 5-nm Cu/Nb multilayers. Note the gradual transition between linear elastic and fully plastic yield behavior at flow stresses in excess of 2 GPa. As a comparison, typical strengths for tool steel are on the order of ~2 GPa. Flow stress measurements indicate good agreement with nanoindentation, using a correlation factor of 2.7. Inset: SEM micrograph of micropillar of 5-nm Cu/Nb multilayer in the prepared condition. Layer interfaces are perpendicular to the cylinder axis.

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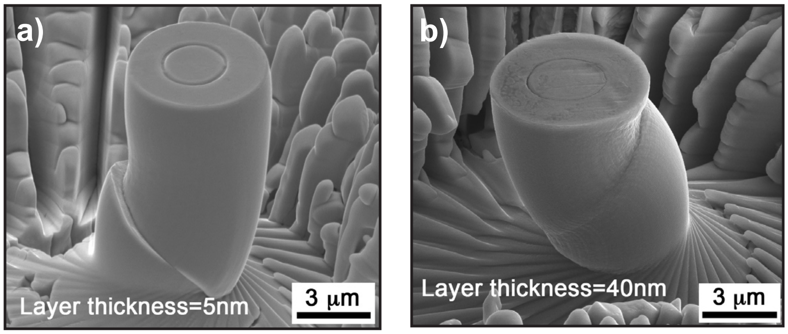

Figure 3. SEM micrographs of micropillars after compression. (a) 5-nm Cu/ Nb multilayer underwent 25% true compresive strain before failing at the shear surface shown. (b) 40-nm multilayer deformed to 35% true compressive strain with failure in shear, but without fracture.

and several configurations, such as larger pillar sizes and different substrates, exhibit similar flow behavior.

The cylinders are compressed at an initial strain rate of $2x10^{-4}$ s^{-1} using a hysitron triboindenter nanoindenter fitted with a 30-µm diameter flat diamond punch, while recording load and displacement data. Using this information, stress-strain curves for Cu/Nb multilayers of 5 nm and 40 nm individual layer thickness are calculated using initial pillar dimensions and are shown in Figure 2. These indicate ductility in excess of 25% in the 5 nm case, at which point the sample failed by a shear instability as is evident in Figure 3a. The maximum flow stress is about 2.4 GPa and is in good agreement with the strength estimated from nanoindentation-measured hardness (σ = hardness/2.7 as a correlation factor as shown in the plot). Preliminary TEM results of deformed pillars indicate the presence of a single-shear band, the formation and propagation of which could explain the softening effect towards the end of the test. 40 nm Cu/Nb mulitlayers exhibit qualitatively the same behavior, albeit at lower ultimate strength and deformability in excess of 30%. The SEM micrograph of the deformed 40-nm-layer-thickness pillar (Figure 3b) shows that a shear instability has formed, leading eventually to sample failure, but the pillar has not fractured.

As microstructural dimensions such as grain size, or as in this study, layer thickness, diminish to below ~10 nm, the fraction of Cu/Nb interface per unit volume of material becomes significant, to the point that deformation behavior is dictated by interface properties rather than by the properties of the constituent bulk Cu or bulk Nb. In the 5-nm Cu/Nb case, this gives rise to single-dislocation deformation mechanisms where the dislocation must cross the Cu/Nb interface. The Cu/Nb interface is unique in that it is incoherent, is resistant to significant interdiffusion even at elevated temperatures, and may have limited shear strength. This limited shear strength can lead to dislocations in Cu being attracted to the interface, where it becomes trapped due to dislocation core spreading. Very large (~GPa) stresses are required to collapse the core and allow transmission into the adjacent Nb layer, leading to the extreme strengths seen in this material. The flow stresses encountered during micropillar compression of the 5-nm Cu/Nb material are approximately 2.4 GPa, which is on the order of those usually seen in tool steel. This is especially remarkable when one takes into consideration that the yield strengths of pure, single-crystal metals, such as Cu and Nb, are ~20 MPa at room temperature. That is, the Cu/Nb nanocomposite exhibits strength of up to two orders-of-magnitude greater than a rule-of-mixtures calculation between its constituents, while maintaining significant deformability.

A detailed TEM study of the deformed Cu/ Nb micropillars, as well as in situ compression in the TEM, is underway to examine the effect of interfacial spacing on the motion of defects, such as dislocations across interlayer boundaries. Future experimental and modeling work will focus on material systems such as Al/TiN or Cu/Ni to investigate effects of interfacial characteristics on mechanical behavior.

This work was funded by DOE/BES and the LANL LDRD/Postdoctoral Research and Development Program.

References

1. N.A. Mara, D. Bhattacharyya, P. Dickerson, R.G. Hoagland, and A. Misra, *Applied Physics Letters* **92**(23), 231901-3 (2008).
2. A. Misra, X. Zhang, D. Hammon, and R.G. Hoagland, *Acta Materialia* **53**(1), 221-6 (2005).
3. N.A. Mara, D. Bhattacharyya, R.G. Hoagland, and A. Misra, *Scripta Materialia* **58**(10), 874-877 (2008).
4. A. Misra, M. Verdier, Y.C. Lu, H. Kung, T.E. Mitchell, N. Nastasi, and J.D. Embury, *Scripta Materialia* **39**(4/5), 555-60 (1998).
5. M.D. Uchic, D.M. Dimiduk, J.N. Florando, and W.D. Nix, *Science* **305**(5686), 986-9 (2004).
6. M.D. Uchic and D.A. Dimiduk, *Materials Science & Engineering A (Structural Materials: Properties, Microstructure and Processing)* **400**/401, 268-78 (2005).